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340 Brannan Street, Suite 305

San Francisco, CA 94107

Ph. (415) 512-8800

Fax (415) 512-8982

Translation from Japanese

(19) JAPANESE PATENT OFFICE (JP)

(11) Japanese Laid-Open Patent Application (Kokai) No. 3-93163

(12) Official Gazette for Laid-Open Patent Applications (A)

(51) Int. Cl.⁵: Classification Symbols: Internal Office Registration Nos.:

H 01 M 4/58
 10/40

8222-5H
Z 8939-5H

(43) Laying-Open Date: April 18, 1991

Request for Examination: Not yet submitted

Number of Claims: 1

(Total of 5 pages [in original])

(54) Title of the Invention: A Nonaqueous Secondary Cell

(21) Application No. 1-227990

(22) Filing Date: September 1, 1989

(72) Inventor: Yoshihiro Furukawa

(72) Inventor: Toshiyuki Noma

(72) Inventor: Yuji Yamamoto

(71) Applicant: Sanyo Denki Co., Ltd.

(74) Agent: Shiro Nakajima, Patent Attorney

SPECIFICATION

1. Title of the Invention

A Nonaqueous Secondary Cell

2. Claims

A nonaqueous secondary cell which contains a negative electrode, for which the active material consists of a lithium or a lithium alloy, and a positive electrode, for which the active material consists of a compound oxide expressed by $\text{Li}_x \text{MnO}_y$ (x and y are positive variables), wherein said nonaqueous secondary cell is characterized by the fact that the amount of sodium in the aforementioned compound oxide has been reduced.

3. Detailed Description of the Invention

(Field of Industrial Utilization)

The present invention concerns a nonaqueous secondary cell in which the negative electrode active material consists of a lithium or a lithium alloy, and in particular concerns an improvement in the positive electrode.

(Prior Art)

Molybdenum trioxide, vanadium pentoxide, titanium or niobium sulfide, and the like have been proposed as the positive electrode active material for this type of secondary cell, and some have been put to practical use.

Manganese dioxide and fluorocarbons, on the other hand, are known as typical examples of positive electrode active material in nonaqueous primary cells, and these have already been put to practical use. Manganese dioxide is particularly advantageous in that it has an exceptional shelf-life, it is an abundant resource, and it is inexpensive.

In light of this background, it is believed that it would be beneficial to use manganese dioxide as the positive electrode active material in nonaqueous secondary cells, but manganese dioxide is problematic in terms of charge-discharge cycle characteristics and there is some difficulty in reversibility.

With the intention of solving the aforementioned drawbacks in the use of manganese dioxide, the present applicants earlier proposed the use, as shown in Japanese Laid Open Patent Application 63-114064, of MnO_2 containing Li_2MnO_3 , of a manganese oxide which contains lithium and whose X-ray diffraction pattern had peaks of $2\theta=22^\circ$, 31.5° , 37° , 42° , 55° in $\text{CuK}\alpha$, or of a manganese oxide having a spinel-type structure, a λ -type structure, or a structure between these two types, as the positive electrode active material.

(Problems Which the Present Invention Is Intended to Solve)

These are all manganese compound oxides which contain lithium and which are expressed by Li_xMnO_y , and because the crystal structure is reversible with respect to the penetration and expulsion of lithium, improvements in cycle characteristics have been observed. Further improvements in other characteristics, however, are desired in terms of practical use.

The present invention was developed in light of such circumstances, and its objective is to offer a nonaqueous secondary cell in which cycle properties could be improved even further.

(Means Used to Solve the Above-Mentioned Problems)

To accomplish the aforementioned objective, the present invention, which is a nonaqueous secondary cell containing a negative electrode, for which the active material consists of a lithium or a lithium alloy, and a positive electrode, for which the active material consists of a compound oxide expressed by Li_xMnO_y (x and y are positive variables), is characterized by the fact that the amount of sodium in the aforementioned compound oxide has been reduced.

(Effect of the Invention)

The present applicants conducted a variety of investigations in order to further improve cell characteristics when an $\text{Li}_x \text{MnO}_y$ compound oxide is used as the positive electrode active material. As a result, it was discovered that the discharge capacity of positive electrode active material greatly increased if virtually no sodium was contained in the manganese dioxide which served as a raw material when an $\text{Li}_x \text{MnO}_y$ compound oxide was synthesized.

Specifically, alkali-based neutralization treatment is generally carried out in the manufacturing process of manganese dioxides which are used as the active material in a cell, and sodium salts are often used as the alkali at this time. It has been ascertained that manganese dioxides in which neutralization treatment has been carried out with the use of a sodium salt usually contain about 1000 to 5000 ppm sodium. Although the reasons have yet to be determined, in an $\text{Li}_x \text{MnO}_y$ compound oxide which has been synthesized by means of heat treatment involving a lithium salt and this type of sodium-containing manganese dioxide, during the calcination reaction the sodium in the manganese dioxide exercises a negative effect on the calcination reaction of the MnO_2 and lithium salt, and discharge capacity consequently diminishes. When charging and discharging are repeated, the sodium in the positive electrode is eluted in the course of the charge-discharge cycle, and due to the fact that [the sodium] is deposited on the negative electrode, the charge and discharge reaction on the surface of the negative electrode is impaired, thus bringing about a deterioration in cycle life.

Based on the results of the aforementioned experiments, it is possible to eliminate the aforementioned negative influence due to sodium if manganese dioxide with a reduced sodium content is used as the raw material during the synthesis of the $\text{Li}_x \text{MnO}_y$ which [serves as] the positive electrode active material, that is, if virtually no sodium is contained in said $\text{Li}_x \text{MnO}_y$.

(Practical Examples)

The practical examples pertaining to the present invention will be described below with reference to Figures 1 through 3 [sic].

Figure 1 is a half section of the nonaqueous secondary cell pertaining to the present invention; a negative electrode 2 which was made of a metallic lithium was press-bonded to the interior surface of a negative electrode current collector 7. This negative electrode current collector 7 was affixed to the inside bottom surface of the negative electrode housing 5 which was made of stainless steel having a C-shaped cross section. The periphery of the aforementioned negative electrode housing 5 was affixed inside of a polypropylene insulative packing 8, and the positive electrode stainless steel housing 4 which had a C-shaped cross section was affixed on the outer perimeter of the insulated packing 8 on the side opposite that of the aforementioned negative electrode housing. A positive electrode current collector 6 was affixed to the inside bottom surface of this positive electrode housing 4, and the positive electrode 1 was affixed to the internal surface of this positive electrode current collector 6. A separator 3 made of a microporous polypropylene thin film was installed between the positive electrode 1 and the negative electrode 2. The cell dimensions were 24.0 mm in diameter and 3.0 mm in width. 1 mol/L of lithium perchlorate was dissolved in a mixed solvent of propylene carbonate and dimethoxy ethane for use as the electrolytic solution.

The positive electrode 1 which constitutes the essential point pertaining to the present invention was manufactured in the following manner.

First, the manganese dioxide which was to serve as the raw material for the Li_xMnO_y compound oxide, which itself was to serve as the positive electrode active material, was manufactured by the procedure indicated below. An MnSO_4 solution (2 mol/L) and an H_2SO_4 solution (2 mol/L) were mixed in equal amounts and an electrolytic solution was thus produced; an electrolytic manganese dioxide was then synthesized using this electrolytic solution (solution temperature: 95°C) and a graphite electrode. The electrical current density at this time was 10 mA/cm². The aforementioned electrolytic manganese dioxide was then thoroughly washed in warm water, 1 L of an NH_4OH solution (0.8 mol/L) was added to 100 g of the electrolytic manganese dioxide, the [resulting mixture] was then stirred in a beaker for 1 hour while being maintained at 60°, and neutralization treatment of the electrolytic manganese dioxide was carried out. The electrolytic manganese dioxide was then washed in cold water, filtered, and dried.

8 g of the electrolytic manganese dioxide obtained in this manner and 20 g lithium hydroxide were blended in mortar then heat treated for 20 minutes at 375°C in air, and a manganese oxide containing Li_2MnO_3 was thus prepared. A positive electrode mix was made by mixing the active material powder obtained in the above manner with acetylene black as a conductor and a fluororesin powder as a binder at a weight ratio of 90:6:4; this positive electrode mix was compression molded at 2 tons/cm² to a diameter of 20 mm, and a positive electrode was then manufactured by heat treating at 250°C. A negative electrode 20 mm in diameter which had been punched from a lithium sheet of a prescribed thickness was used.

The cell manufactured in this manner is designated below as cell A₁.

(Practical Example 2)

A cell was manufactured in the same manner as in Practical Example 1 except that, during the manufacturing process of the aforementioned electrolytic manganese dioxide described in Practical Example 1, neutralization treatment was carried out using an LiOH aqueous solution (0.8 mol/L) instead of the NH_4OH aqueous solution (0.8 mol/L).

The cell manufactured in this manner is designated below as cell A₂.

(Practical Example 3)

A cell was manufactured in the same manner as in Practical Example 1 except that, during the manufacturing process of the aforementioned electrolytic manganese dioxide described in Practical Example 1, no neutralization treatment based on an NH_4OH aqueous solution was carried out.

The cell manufactured in this manner is designated below as cell A₃.

(Practical Example 4)

During the manufacturing process of the aforementioned electrolytic manganese dioxide described in Practical Example 1, neutralization treatment of the manganese dioxide was carried out using an NaOH aqueous solution (0.8 mol/L) instead of an

NH_4OH aqueous solution, and a sodium removal treatment was carried out by stirring the manganese dioxide for 8 hours in 1 L of an H_2SO_4 aqueous solution (0.5 mol/L). Next, the manganese dioxide was washed in cold water and then neutralized for 1 hour in 1 L of an NH_4OH aqueous solution (0.8 mol/L). An electrolytic manganese dioxide was then manufactured by washing again in cold water, filtering, and drying. Other than preparing the electrolytic manganese dioxide in this manner, a cell was manufactured in the same manner as in Practical Example 1.

The cell manufactured in this manner is designated below as cell A_4 .

(Practical Example 5)

During the manufacturing process of the aforementioned electrolytic manganese dioxide described in Practical Example 1, neutralization treatment was carried out using an NaOH aqueous solution (0.8 mol/L) instead of an NH_4OH aqueous solution. The manganese dioxide obtained in this manner was then stirred for one hour in 60°C warm water (1 L), filtered, then stirred for another hour in 60°C warm water (1 L). This warm water sodium removal treatment was repeated for a total of 8 times and an electrolytic manganese dioxide was obtained. A cell was manufactured in the same manner as in Practical Example 1 except that the electrolytic manganese dioxide was prepared as above.

The cell which was manufactured in this manner is designated cell A_5 .

(Comparative Examples)

A cell was manufactured in the same manner as in Practical Example 1 except that neutralization treatment was carried out using an NaOH aqueous solution (0.8 mol/L) instead of an NH_4OH aqueous solution during the manufacturing process of the electrolytic manganese dioxide described in Practical Example 1.

The cell manufactured in this manner is designated below as cell X.

(Experiment 1)

An examination was made of the initial discharge capacity and the sodium content in the electrolytic manganese dioxide used in the manufacture of the positive electrode active material in the aforementioned cells A₁ through A₅ pertaining to the present invention, and in cell X of the comparative example; the results are shown in Table 1 below. The testing conditions for initial discharge capacity were such that discharge was conducted at 3 mA up to 2.0 V.

Table 1

| Cell type | Sodium content (ppm) | Initial discharge capacity (mAh) |
|-----------|----------------------|----------------------------------|
| Cell A1 | 50 | 48 |
| Cell A2 | 50 | 46 |
| Cell A3 | 200 | 41 |
| Cell A4 | 500 | 36 |
| Cell A5 | 800 | 33 |
| Cell X | 5000 | 29 |

As indicated in Table 1 above, it may be observed that the sodium content of the electrolytic manganese dioxide used in cells A₁ through A₅ pertaining to the present invention was 50 to 800 ppm, indicating a low level, whereas the sodium content in the electrolytic manganese dioxide used in cell X of the comparative example was 5000 ppm, indicating a high level. It may be observed in particular that when no sodium salt was used in the neutralization treatment during the manufacturing process of the electrolytic manganese dioxide, the sodium content was 50 to 200 ppm, indicating a remarkably low level.

The sodium content in the manganese dioxide was generally 1000 ppm or less when neutralization treatment was not carried out with sodium salt, and the use of manganese dioxide having a sodium content in this range is desirable; it can be seen that the sodium content of the electrolytic manganese dioxide used in the aforementioned cells A₁ through A₅ was in all cases under 1000 ppm and was thus within that range.

It may be observed that the initial discharge capacity was 33 to 48 mAH in cells A₁ through A₅, whereas it was only 29 mAH in cell X. It was observed in particular that [initial discharge capacity] was over 40 mAH in all of cells A₁ through A₃ in which the sodium content was under 200 ppm. It is therefore desirable to manufacture a positive electrode using a manganese dioxide having a low sodium content.

(Experiment 2)

The charge-discharge cycle characteristics of cells A₁ through A₅ pertaining to the present invention, and of cell X, were investigated; the results are shown in Figure 2. Testing conditions were such that discharging took place for 4 hours at 3 mA, after which charging took place at 3 mA up to a 4 V charge termination voltage.

As shown in Figure 2, it was observed that discharge termination voltage did not begin to deteriorate substantially through 100 cycles in cells A₁ through A₅, whereas in cell X discharge termination voltage began to deteriorate in less than 100 cycles. It was observed in particular that especially favorable characteristics were exhibited by cells A₁ through A₅ in which manganese dioxide having a low sodium content was used.

In the aforementioned practical examples, electrolytic manganese dioxide was used as a raw material in an Li_xMnO_y positive electrode active material. It is obvious that the present invention is not limited just to this [particular instance]; chemical and natural manganese dioxide can also be suitably used.

Neither is the present invention limited only to the aforementioned nonaqueous secondary cells; it can also be applied to nonaqueous secondary cells in which solid electrolytes are used.

(Merits of the Invention)

As described above, it is possible both to increase initial discharge capacity and to bring about dramatic improvements in cycle characteristics if the sodium content in a compound oxide is reduced. It is accordingly proposed that dramatic improvements in cell performance can be brought about.

4. Brief Description of the Figures

Figure 1 is a half section of the cell pertaining to the present invention, and Figure 2 is a graph showing the cycle characteristics of cells A₁ through A₅ pertaining to the present invention and of cell X.

1:positive electrode; 2:negative electrode; 3:separator.

Figure 1

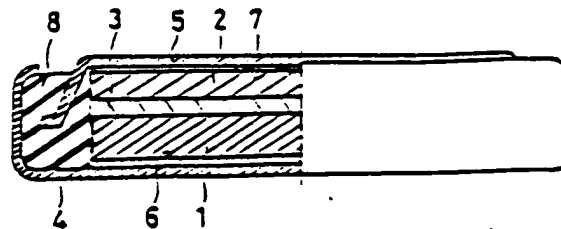


Figure 2

